2.0 INTRODUCTION

The majority of prior research devoted to pollution prevention in the vital semiconductor industry has focused on the replacement of ozone-depleting chlorofluorocarbon (CFC) precision cleaners and solvents with environmentally-benign chemicals which can function in the same capacity. With the guidance of such entities as SEMATECH (SEmiconductor MAnufacturing TECHnology, a research consortium of the 10 largest U.S. semiconductor manufacturers) and successful development programs by the industrial vendors, a host of proven replacements have been developed and are beginning to be implemented throughout the semiconductor manufacturing industry. Ongoing efforts in this area will undoubtedly continue as further improvements in cleaning processes are tested and marketed.

However, there are ongoing environmental threats in certain types of semiconductor manufacturing that have been largely ignored until the present. For example the toxic element arsenic is widely used as a principle component in important semiconductor substrates such as GaAs and as a dopant for modifying the electronic characteristics of other substrates. At present, much of the waste produced in arsenic-based semiconductor manufacturing goes to land disposal, while arsenic-laden wastewaters produced in some operations are released (at low concentrations) to local POTWs. Arsenic is a relatively low cost material and by itself, offers little economic incentive for the implementation of pollution prevention.

There is, however, an incentive for the development of waste minimization and materials substitution practices because of the ongoing use of certain, relatively scarce materials (e.g., gallium and indium) in arsenic-containing semiconductor device manufacturing procedures. The worldwide scarcity of such materials, as well as the lack of any domestic ores or suppliers, implies that the U.S. semiconductor industry must continue to pay high prices for imported raw materials. A number of very possible political or economic scenarios in foreign countries (or even in the U.S.) could drive the price of these materials to exorbitant levels, or could cause them to become essentially unavailable. Therefore, these materials truly can be classified as "strategic" metals, because of their use in a high technology, defense-related capacity, as well as their overall availability.

This report includes an introduction to the current status of the U.S. semiconductor industry from a materials-related pollution prevention standpoint. The U.S. Environmental Protection Agency (U.S. EPA) has an interest in the minimization of wastes (such as arsenic) from semiconductor manufacturing operations, while at the same time doing so in a way that will not hamper this important industry. Under the subject project, the University of Dayton Research Institute (UDRI) has conducted specific research into pollution prevention and waste minimization methods for this industry from a materials recovery perspective.

2.1 WHY ARSENIC AND OTHER TOXIC ELEMENTS ARE IMPORTANT IN SEMICONDUCTOR DEVICE MANUFACTURING

Silicon (Si) has been, and will continue to be, the dominant material used for the overwhelming majority of semiconductor device applications. Silicon itself is environmentally-benign, and is toxic only when in the form of gaseous silane or as certain organosilanes. In the last ten to twenty years, however, there has been a tremendous upsurge in the use of compound semiconductors (i.e., semiconductors whose crystalline structure contains two or more elements) for both commercial and military applications, as these materials have moved from the laboratory to specific applications. The usage and demand for compound semiconductors will continue to increase, in much the same way that the demand for silicon-based devices has continued to increase. Many of these compound semiconductors utilize chemical elements or precursor materials that exhibit varying degrees of toxicity (e.g., arsine, phosphine, stibine, etc.) For this reason, compound semiconductors present an opportunity to perform pollution prevention and waste minimization on a materials recovery and reuse basis.

2.1.1 Compound Semiconductors in Use Today

Table 2-1 presents a very general summary of the compound semiconductors which are in use today, or which are rapidly approaching widespread acceptability. Arsenic, as a group V element, is used in the manufacture of certain so-called III-V compound semiconductor materials (i.e., semiconductors composed of elements from group III and group V of the periodic table). The last three "families" shown in Table 2-1 have not as yet made a significant impact on the U.S. semiconductor industry, but should be expected to do so within the next ten to twenty years. The first three compound semiconductor families already are in widespread use.

The III-V semiconductors are used in a multitude of device applications, including light-emitting diodes (LEDs), lasers, detectors, and communication devices. For example, every cellular phone presently utilizes a gallium arsenide (GaAs) chip because the transfer of electrons through GaAs results in microwave oscillations. Because III-V pnictides can be readily alloyed with one another, it is possible to fabricate light emitters or detectors capable of functioning from far-infrared through green spectral wavelengths. And, with the continuing development of nitride-based devices (e.g. GaN, AlN), it will very soon be possible to fabricate solid-state devices that can function well into the ultraviolet.

The majority of II-VI semiconductors have traditionally been used for photovoltaic applications, wherein light energy is converted into electrical current. Mercury cadmium telluride (HgCdTe), when cooled to liquid nitrogen temperatures, is an excellent detector for use in the far-infrared spectral regime, and as such, is used on satellites for weather or spy applications. The IV-VI chalcogenides such as lead sulfide (PbS) are also utilized as infrared detector devices.

Table 2-1
Compound Semiconductors

Compound Family	Semiconductor Examples	U.S. Production/Usage
III-V	GaAs, InP, InSb, GaP, GaN	Large
II-VI	CdS, CdSe, HgCdTe, ZnSe	Large
IV-VI	PbSe, PbS	Medium
IV-IV	SiC, Si-Ge	Small
I-III-VI2	CuInSe2	Small
II-IV-V2	ZnGeP2	Small

2.1.2 Toxic Elements and Precursors Used in Compound Semiconductor Fabrication

Lead, mercury, and cadmium have been targeted by the Pollution Prevention Act as being among seventeen chemicals for which waste reduction options must be attempted for those manufacturing entities that utilize them. Therefore, fabricators of cadmium- and mercury-based II-VI compounds, as well as lead chalcogenide devices, are required to seek methodologies to reduce emissions of these chemicals.

In addition to these three chemical elements, arsenic and selenium are currently regulated under such legislation as the Drinking Water Act. Therefore, disposal of wastes containing lead, cadmium, mercury, arsenic, or selenium carries the potential for future legal liabilities. Somewhat less toxic species such as antimony, copper, zinc, or tellurium also may be regulated on a state or local basis. Finally, it must be remembered that dopant or epitaxial sources may also be regulated. An example of the former includes beryllium; examples of the latter include phosphine (PH3), ammonia (NH3), silane (SiH4), or hydrogen sulfide (H2S).   Many of these epitaxial sources are among the most toxic substances known to man. For example, the dopant and epitaxial source arsine (AsH3) is instantly lethal in concentrations of only 250 parts per million in air. Lower concentration exposures result in chronic effects and often subsequent death.

2.2 "STRATEGIC" ELEMENTS USED IN SEMICONDUCTOR DEVICES

The U.S. semiconductor industry currently imports the majority of its silicon from Australia, due to the high purity reserves that are present in that country. If needed, the industry could turn to lower-grade, domestic reserves for its source of silicon. There are, however, three chemical elements that must be classified as "strategic" because of the current lack of domestic reserves or suppliers, their worldwide scarcity, and their important use in U.S. defense-related applications. These are gallium, indium and germanium. Of these, gallium and indium are currently utilized almost exclusively in III-V semiconductor applications, although the future will also see their use in I-III-VI2 semiconductors. Germanium was one of the first semiconductors used for communications; its use in "cats-whisker" crystal radios even predated our understanding of semiconductors.   However, newer semiconductor applications (e.g. gallium-doped germanium, silicon-germanium, and II-IV-V2 compounds) are causing a revival of its usage. It must also be remembered that these three chemical elements have other, albeit

specialized applications - gallium in magnesium gallate phosphors for photocopying, germanium in bismuth germanate scintillators for astral sensor devices, and indium for specialized plating applications. A true appreciation of the relative scarcity of these materials and the precarious U.S. supply situation can only be realized by quickly reviewing the sources (or lack thereof) for each of these three chemical elements.

Gallium (Ga) Sources

In terms of its abundance in crustal rocks, gallium is not that rare a chemical element, being 30th in terms of abundance at an average concentration of 19 ppm. However, what makes gallium so rare in terms of availability is that it is very uniformly distributed throughout a large number of rocks at these concentrations. Thus, there are no concentrated ores from which gallium can be extracted, as is often the case with many chemical elements which are present in lower concentrations in crustal rocks, such as silver, gold, or the platinum metals. There are no gallium-containing minerals of any economic significance. The few minerals that do contain appreciable concentrations of gallium (e.g. germanite and gallite) are so rare that they can be considered nothing more than mineralogical curiosities.

Contacts made with semiconductor manufacturers indicated that the U.S. semiconductor industry obtains most of its high-purity gallium from either Japan or Germany. Gallium is concentrated as a result of the processing of other materials whose ores contain low concentrations of gallium and thus is derived from wastes of other industrial processes, such as flue dusts from the zinc industry or sludges from the aluminum industry. For example, bauxite (the primary aluminum ore) typically contains 0.003 to 0.01% Ga. Concentrations in zinc ores (e.g. sphalerite) are comparable. Because of such scarcity, industry sources say that the price of semiconductor grade gallium recently has ranged from $0.50 to $1.50 per gram.

Indium (In) Sources

Like gallium, there are no indium minerals of any economic significance. Those indium minerals that do exist in nature (e.g. roquesite, indite, and dzhalindite) are exceedingly rare. Indium is one of the rarest of the commonly-used compound semiconductor constituents in terms of its crustal abundance (61st in abundance at an average concentration of 0.24 ppm). However, from a practical standpoint, it is more readily available because it occurs not only in zinc and tin ores, but also in association with lead, iron, and copper sulfide. Therefore, indium can be derived from the flue dusts and sludges of these industries. High purity indium for semiconductor fabrication is most often obtained from Germany or Japan, at an average cost of $50 to $150 per kilogram, depending on purity.

Germanium (Ge) Sources

Germanium is also a rare element in the earth's crust, being 53rd in order of abundance at an average concentration of 1.5 ppm. As with gallium and indium, no

significant ores or minerals exist for commercial mining, and germanium minerals (e.g. germanite, argyrodite, argutite, renierite, and briartite) are merely collector items. At present, germanium is principally derived from flue dusts from the zinc or tin industries, and, according to manufacturers, its cost approaches $300 per kilogram in raw, unpurified form.   One of the highest natural concentrations of germanium is in coal (0.01%), and coal ashes can contain up to 1% germanium as GeO_2. Some work was conducted by the British in the 1950s and 1960s to develop methodologies for the extraction of germanium from coal ash, but there are no such sources being used in the U.S. at present.

2.3   GENERAL SUMMARY OF MANUFACTURING PROCESSES FOR COMPOUND SEMICONDUCTORS

The ultra-precise manufacturing steps involved in fabricating semiconductor components from raw materials represents one of the greatest achievement by materials science and chemistry to date. In order to achieve materials with the final desired electrical characteristics and properties, a large number of manufacturing steps are necessary. Although the exact manufacturing steps are largely governed by the final desired properties of the material, as well as the initial starting materials, a general overview of the manufacturing steps can be summarized (Figure 1.1). These include:

- Growth of bulk substrate crystals;
- Cutting, polishing, and etching of substrates;
- Epitaxial growth of circuit constituents on substrate (if desired);
- Multisequenced masking and doping of atoms into substrate (if desired);
- Metallization;
- Alloying/annealing; and
- Final lapping and separation of individual semiconductor "chip" devices.

Typically, the first three operations are performed at facilities that grow the initial crystal of semiconductor material. These crystal growers are referred to as semiconductor "foundries" and they provide the basic substrates on which specific devices can be "grown" in a controlled manner. Subsequent operations are then carried out by one or more specialty device manufacturing houses until semiconductor "chips" are prepared for the final user market.

Of course, each one of these general processes may involve numerous preparation and handling steps. Also, all of these steps may not be necessary for the fabrication of a specific electronic component, or the order in which they are carried out may be varied. Each of these manufacturing steps is summarized below, with a particular emphasis on the types of input materials used, as well as waste products that are typically generated. Finally, it should be remembered that the conclusion of each of these manufacturing steps represents a quality control checkpoint from the standpoint of meeting product quality
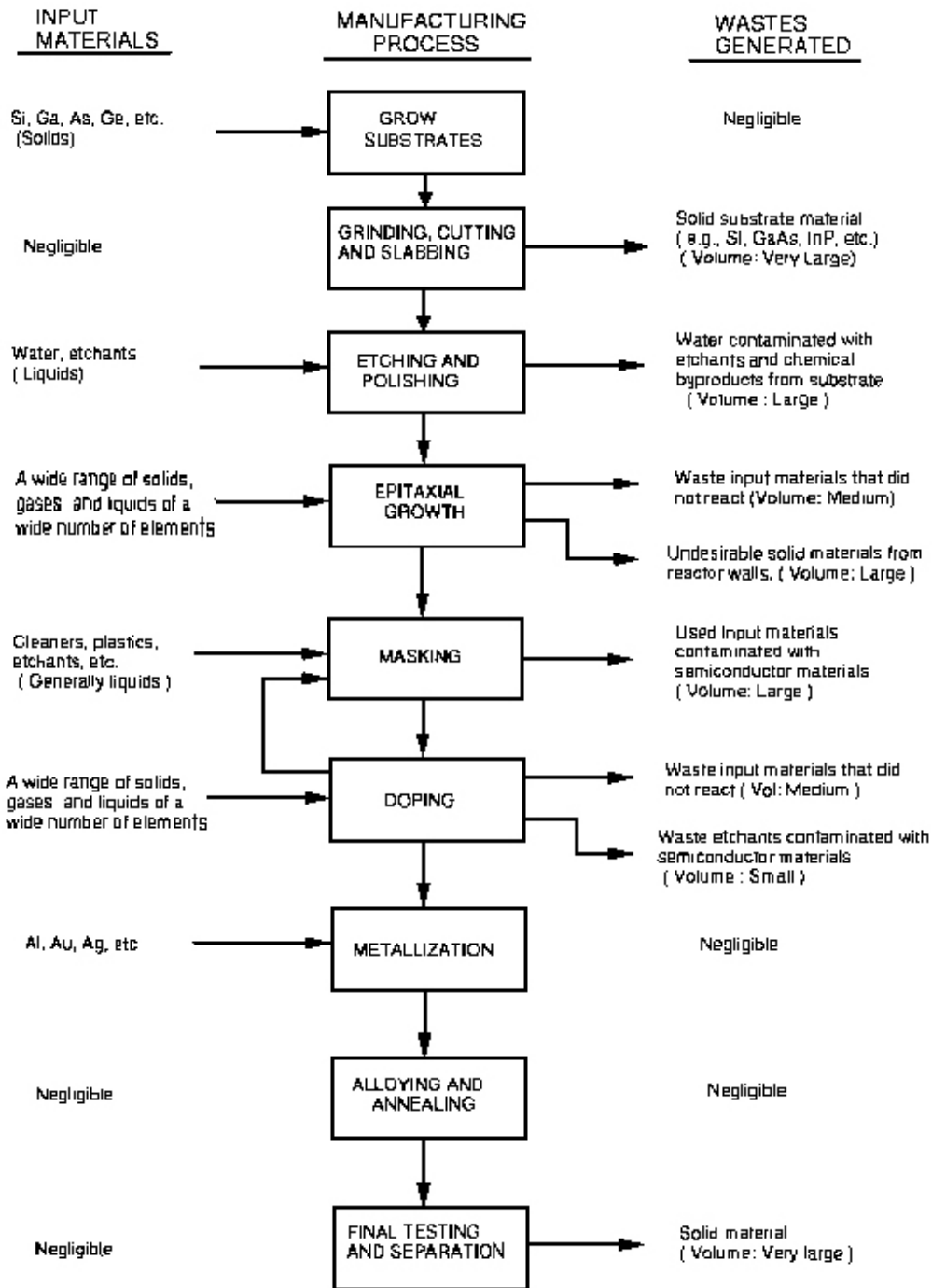
INPUT MATERIALS	MANUFACTURING PROCESS	WASTES GENERATED
Si, Ga, As, Ge, etc. (Solids)	GROW SUBSTRATES	Negligible
Negligible	GRINDING, CUTTING AND SLABBING	Solid substrate material (e.g., Si, GaAs, InP, etc.) (Volume: Very Large)
Water, etchants (Liquids)	ETCHING AND POLISHING	Water contaminated with etchants and chemical byproducts from substrate (Volume : Large)
A wide range of solids, gases and liquids of a wide number of elements	EPITAXIAL GROWTH	Waste input materials that did not react (Volume: Medium)
		Undesirable solid materials from reactor walls. (Volume: Large)
Cleaners, plastics, etchants, etc. (Generally liquids)	MASKING	Used input materials contaminated with semiconductor materials (Volume: Large)
A wide range of solids, gases and liquids of a wide number of elements	DOPING	Waste input materials that did not react (Vol: Medium)
		Waste etchants contaminated with semiconductor materials (Volume : Small)
Al, Au, Ag, etc	METALLIZATION	Negligible
Negligible	ALLOYING AND ANNEALING	Negligible
Negligible	FINAL TESTING AND SEPARATION	Solid material (Volume: Very large)

Figure 2.1 - Process Flow Diagram for Compound Semiconductor Device Fabrication
(Note-volume descriptors are relative and specific to a particular semiconductor)

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objectives. Any devices that do not meet specifications at each of these points will be discarded. Such discards are a significant contribution (at least at the present time) to the overall semiconductor waste stream.

2.3.1 Growth of Bulk Substrate Crystals

The quality of bulk substrates is an important aspect of electronic device design. Significant improvements have been made in the areas of bulk crystal growth with regard to uniformity, reproducibility, thermal stability, diameter control, and impurity and dopant control. Substrate crystals of silicon or germanium have conventionally been prepared by either the Czochralski or float-zone methodologies. However, compound semiconductors, because they involve the joining of two or more elements, must use more sophisticated techniques. Although many different methodologies are currently being used in the industry today, two examples stand out as being representative of these methodologies. The horizontal gradient freeze technique is a static technique where the melt is gradually solidified by movement of a temperature gradient along the melt. Vertical Bridgeman furnaces utilize a similar temperature gradient movement (in a vertical direction, however) to achieve controlled crystal growth. Average growth rates using these methodologies are from 1 to 5 mm per hour. Typical crystal dimensions produced by these methodologies range from one to six inches in diameter, and from two to thirty inches in length.

The actual growth of bulk crystals (also called boules or ingots) generates very little waste, since starting materials are fed into the system in exact quantities. Should excess starting materials result, then they are almost always reused in the production of other crystalline boules. While a defective boule would represent a significant mass of waste materials, their incidence of occurrence is very low, and even if a defective boule were to be generated, usable portions of the material are frequently salvaged.

2.3.2 Cutting, Polishing, and Etching of Bulk Crystals

The semiconductor boule obtained has a generally cylindrical shape with somewhat conical ends. After removing the ends (which, since they have smaller diameters than required are usually wasted), the first operation is often surface grinding. This process is used to precisely define the diameter of the material and is accomplished using a rotating cutting tool (i.e., a lathe) that makes multiple passes down the rotating boule until the desired diameter is obtained. A flat is then ground along the entire length of the ingot, and the surface orientation is determined by cutting several slices and measuring their crystalline orientation using an x-ray diffraction method. The cutting saw is then reset so that the proper orientation (i.e., the desired crystal faces) is achieved for subsequent cutting of wafers.

Upon proper orientation, the crystal is cut into thin slices called wafers. The slicing is accomplished using either of two common wafer sawing procedures. In one procedure, the inside diameter of a ring-shaped saw blade made of stainless steel with diamond impregnated on the inner rim. Newer, more efficient methods, utilize a series of

rapidly moving abrasive-coated steel wires over the ingot, so that multiple cuts can be performed simultaneously. Both such cutting processes are liquid cooled, and a volume of material is lost during this process equal to the width of the saw blade or wire. In fact, approximately one-third of the total crystal mass can be lost as sawing fines during the cutting process. This waste stream is in the form of fine powders suspended in an oil or water matrix (depending on the coolant liquid used for the cutters.) The sawing operation also leaves a damaged layer of about 20 to 50 microns thick on the wafer that is later removed by lapping and etching.

2.3.3 Wafer Lapping, Etching and Polishing

The final operation performed at a crystal foundry is polishing. The wafers are mounted onto large circular stainless steel polishing plates (lap plates), and either wax or vacuum is used to hold them in place. These plates are then mounted on a polisher, and the wafers are pressed against a tough polishing pad. A polishing agent such as alumina and an etchant that contains a chemical oxidizer are used simultaneously, and the surfaces are continuously flushed with water as they are polished. The etchant (oxidizer) is used to aid in polishing by slowly dissolving some of the semiconductor material from the surface being polished. Either one or both sides of the wafer are polished to a mirror-like finish. After a thorough cleaning and subsequent inspection, the wafers are ready for device fabrication.   Device fabrication usually is performed at specialty job-shops, while only the early stages of semiconductor manufacturing (i.e., boule growth, wafer cutting and polishing) are performed at semiconductor foundries.

The high percentage of wastes associated with foundry operations makes their wastes the largest mass of waste for the compound semiconductor industry. Toxic wastes from these operations can be loosely categorized into two forms:

1. liquid wastes that contain dissolved metal ions from the etching and polishing operations, and

2. solid wastes, i.e., large pieces and cutting fines from the cutting and shaping operations.

The wastes from crystal polishing consist of the flushant wastewaters containing dissolved substrate materials with suspended polishing agent. For example, the polishing wastewaters from GaAs manufacturing contain dissolved arsenic and dissolved gallium at concentrations of between 200 and 400 ppm. These wastewaters are difficult to treat because of stringent arsenic discharge limits and because of the difficulties introduced into any sludge dewatering operations by the extremely fine, suspended polishing agent particles.

Solid wastes from cutting can range in size from whole segments of ingots (e.g. 6" diameter wafer pieces) to fine powders of a few microns in size suspended in the saw's coolant liquid. Out-of-spec wafers (along with the discarded boule ends and ingot segments) compose another form of solid wastes generated at semiconductor foundry

operations. These latter solid wastes are physically large and are of high purity. Thus, they have been the only part of a foundry's waste stream that has been captured for recovery and reuse. Often, these wastes are sent to off-site contractors who process the waste for recovery of gallium alone (with any arsenic being wasted). No effort has previously been made to recover materials from the sawing fines or from the polishing wastewaters.

2.3.4 Epitaxial Growth

Epitaxial growth is the means whereby ultrathin layers of exact chemical composition are laid down on substrate wafers that have been prepared by the methodologies described above. In particular, this is a useful means to prepare semiconductors that are to be used for laser or LED applications. There are four general means by which epitaxy can be achieved. These are:

- Liquid-phase epitaxy (LPE);
- Vapor-phase epitaxy (VPE);
- Organometallic vapor-phase epitaxy (OMVPE); and
- Molecular beam epitaxy (MBE).

LPE was the first commercially used epitaxial growth process and it involves the growth of an epitaxial layer on a single crystal substrate from a solution saturated or supersaturated with the material to be grown. VPE utilizes vaporized metal chlorides or hydrides that are transported under controlled conditions (e.g., temperature, pressure, flow rate) to the metal substrates. Unlike the LPE processes, smooth surfaces are attainable, and several processing runs can be performed in an eight hour day. Unfortunately, the toxicities associated with the hydride species used are always high. OMVPE is an improvement over VPE because the reactions are irreversible and this allows very abrupt transitions in composition of epitaxial structures. Such structure is a necessity for the fabrication of digital or analog alloy systems. Another advantage is that lower temperatures can be used for the growth processes and this minimizes the effects of interdiffusion. Additionally, the organometallic substances used in OMVPE are less toxic than hydrides resulting in lower toxicity starting materials and waste products alike. MBE is the process of depositing epitaxial films from molecular or atomic beams on a heated substrate under ultrahigh vacuum (UHV) conditions. The beams are thermally generated from elemental feedstocks in Knudsen-type effusion cells. The thermal beams travel in rectilinear paths to the substrate where they condense and grow under kinetically controlled growth conditions.

With the exception of LPE, the wastes generated from epitaxial growth processes are gaseous or solid in nature. The gaseous wastes are the "exhaust" vapors that are drawn off from the epitaxial reactors. These are either passed through "hot boxes" where they are mixed with oxygen and burned, or are oxidized using often proprietary catalyst materials. Typically, the oxidized gases are scrubbed out of the effluent gas stream and added to the plant's wastewaters for treatment. These waste materials are disposed of with little or no effort directed towards recovery. It is reported that epitaxial growth

processes utilize only 20 to 25 percent of the input materials for final product fabrication. Such process "efficiency" is dependent upon both the design of the reactor and the product being fabricated. For example, existing nitride fabrication systems utilizing ammonia feedstocks frequently operate at only 1% efficiency in terms of input ammonia.

Solid wastes constitute those materials that are deposited on the epitaxial system's reactor walls. It is frequently necessary to remove these wastes prior to the next fabrication run because their presence could interfere with achieving the requisite partial pressures necessary for each constituent in the subsequent run. In fact, fully 50 percent of the labor hours associated with such epitaxial growth processes is devoted to cleaning waste solids off of walls and other reactor parts. This material is not currently recycled back into the overall manufacturing scheme partly because it is usually contaminated with dopant and maskant materials.

2.3.5 Masking and Doping

For establishing specific circuits on a chip, it is common to add dopant atoms into the substrate or to add epitaxial layers in specific configurations in order to produce regions of controlled electronic behavior. This is done by first masking those regions for which no dopant atoms are desired, and then using doping techniques for the regions that are still exposed.

Masking can be divided into two distinct processes, both of which are necessary for the successful transfer of an image to the surface of a semiconductor wafer. These processes include the generation of the "mask", whose image is transferred to the wafer; and the process of transferring the image from the mask to the surface of a wafer through the use of a sensitized layer called a photoresist. Masking results in aqueous streams that may have measurable concentrations of metals that had been deposited on the photoresist when the photoresist is subsequently removed from the substrate wafer with chemical agents.

Doping involves the emplacement of dopant atoms into selected regions of a semiconductor crystal and this is accomplished using either diffusion doping or ion implantation. Diffusion doping involves two distinct processes: predeposition, wherein a carefully controlled amount of dopant is placed onto the surface of the semiconductor; and drive-in, which uses a thermal process to cause diffusion of the dopant into the overall crystal bulk. Today, most doping is effected using a technique called ion implantation. This process takes ions of a desired dopant, accelerates them using an electric field, and scans this "ion beam" across a wafer to obtain a uniform predeposition with subsequent thermal drive-in. Older doping operations generated wastes similar to those described under epitaxial deposition. Ion implantation techniques generate far less wastes.

2.3.6 Metallization/Alloying/Annealing

After the devices have been fabricated, they must be connected together to perform electronic circuit functions. The process of implanting electrical connections is called metallization. Alloying and annealing involve a low temperature heating to ensure low-resistance contact between the deposited metal and the fabricated electronic devices. These processes generate little toxic waste.

2.3.7 Final Lapping and Separation

The backside of a wafer may have to be altered in order to prepare it for subsequent processing steps. Backside lapping of a wafer is used to remove diffused layers that interfere with the electrical properties, to thin the wafer, or to prepare the backside for subsequent metal deposition. When lapping the backside of wafers, approximately ten thousandths of an inch of material is removed from each wafer. This results in fine powders in a water carrier. Currently, these powders are filtered or settled out of solution, and are subsequently land disposed.

The wafers are now ready for final quality control testing. To determine their acceptability, the wafers are placed on a probe and each microchip device on the wafer is tested. Those devices on the wafer that function properly are left alone; those that fail are typically marked with a spot of ink. Separation into individual devices is then achieved with a wafer scribe. This ultrathin saw or laser separates the substrate material into square or rectangular components. Any device that does not function properly is discarded. Finally, there is a large wastage of edge material from each wafer. Because each wafer is round (from the crystal growing process), and because the devices themselves are square or rectangular, there will be some solid waste generated when the devices are separated, even if all devices contained on it pass performance inspections.

2.4 SUMMARY OF POLLUTION PREVENTION PROCESSES DEVELOPED
     UNDER THIS RESEARCH EFFORT

It can be seen that in its current state, the U.S. semiconductor industry offers a multitude of opportunities for waste reduction. Indeed, although the industry itself is perceived as "clean", due to the ultrahigh purity required of input materials and processing equipment, the amount and nature of the waste materials are "dirty" in comparison to many other manufacturing industries. The semiconductor manufacturing industry has devoted most of its resources to building better devices and electronic circuit components, and not to minimization of wastes. Because of the high value of part of their waste streams, combined with the environmental threats posed by other parts of their wastes, U.S. semiconductor fabricators have a very real (but currently unrecognized) economic incentive to implement pollution prevention and waste minimization strategies.

Current Superfund and RCRA legislation makes generating companies liable for environmental cleanup at waste disposal sites, even if wastes have been manifested and disposed in an approved manner. In addition, even though many of the wastes currently

being disposed are unlisted (e.g., GaAs is not a specifically regulated waste except in California) and usually will pass a TCLP test, the toxic metals contained therein still can constitute an environmental threat. In such circumstances, disposal of wastes that contain toxic metals can carry with it potential legal liabilities for environmental cleanup, even if the wastes themselves are unlisted. Finally, shipment of wastes to off-site "recyclers", wherein "strategic" metals are recovered, but toxic species are not, still leaves some legal responsibility with the generating, semiconductor manufacturer should any uncontrolled release (e.g., of unrecycled arsenic) subsequently occur.

The industry's process lines are currently geared towards the manufacture of ultra-precise, miniaturized components, but not towards the recovery of waste fractions. The industry generally views the many processing steps associated with device fabrication (as well as the procedures necessary for environmental compliance) as a cost of doing business, and this cost is passed on to the customer. When compared to other U.S. manufacturing schemes, the overall process efficiencies are terribly low. For example, just in the first three unit operations shown in Figure 1.1 (the crystal foundry operations), total material wastage is approximately 50 percent of the original input material.

At the device fabrication operations (i.e., unit operation four and beyond in Figure 1.1), only about 17% of their input materials (wafers) will ultimately be usable as final devices. In other words, for the entire process, from original crystal growth to final device testing and separation, only approximately 8.5% of the input materials will be used in final electronic components. The remaining material (nearly 92 percent) is currently discarded as wastes.

In spite of the very large apparent paybacks associated with implementation of pollution prevention and waste minimization in the industry, there are certain characteristics unique to U.S. semiconductor manufacturing operations that need to be addressed. These characteristics set the industry apart from other manufacturing operations in the U.S.

2.4.1 Material Substitution Difficulties

In many manufacturing operations, substitution of environmentally-benign materials for toxic or harmful materials has been and is being conducted. Indeed, the successful replacement of CFC precision cleaners by other agents or processes in the semiconductor industry has resulted in a significant decrease in regulated emissions. However, replacement of "toxic" semiconductors (e.g. those compounds containing lead, cadmium, mercury, arsenic, or selenium) or "strategic" semiconductors (e.g. those containing gallium, germanium, or indium) with less toxic or lower-cost semiconducting compounds would be a far more time-consuming process than for other manufacturing operations. For example, it is theoretically possible that the III-V compound semiconductor material aluminum antimonide could be grown and doped to perform many functions of more expensive and more toxic equivalent III-Vs, but there are difficulties associated with such material replacement concepts.

The development period for semiconductor compounds and devices is far longer than for most products developed by other manufacturing industries. For a given semiconductor compound, the development period is measured in terms of years (e.g., twenty years) as opposed to months for most other manufactured products. And, because the semiconductor industry is so interconnected in terms of small companies (see below), validation of the effectiveness of replacement compounds and devices would be needed across a number of manufacturing firms.

This is not to say that materials substitution is not possible in terms of replacement compounds. Rather, it is the opinion of the authors that one of two scenarios would be necessary in order to overcome the development time necessary to bring a new product on-line, and to gain industry acceptance. In one such scenario, if a replacement product already had a long history of development work having been performed on it, this would significantly shorten the development time necessary for device development, and may also help to foster industry acceptance. An example would be the material aluminum antimonide mentioned above. Conceivably such material could replace higher-cost, higher toxicity III-V materials such as GaAs and InP for some device applications, and aluminum antimonide does have a long history of development work associated with it. Under a second scenario, if the materials to be replaced were still "new" in terms of their industry implementation, then waste minimization efforts could more readily be incorporated into production schemes. An example would be the III-nitride wide band gap devices that are just beginning to see large-scale industrial application. Because this industrial sector is still so "new", it is still possible to implement good waste minimization and pollution prevention practices without seriously affecting the industry's concepts about "proper" manufacturing methods.

2.4.2 Difficulties with Small Company Size

A further impediment to implementing pollution prevention in the U.S. semiconductor industry is the fact that unlike many other manufacturing schemes, the entire processing operation is not done under a few, relatively large roofs. Rather, the industry consists of many small "fab-shop" companies performing one or two of the manufacturing steps shown in Figure 1-1, and then selling their products to companies which are involved in additional fabrication operations further down the overall manufacturing scheme. Pollution prevention implementation must therefore enlist the cooperation of several companies in order to be effective for the whole industry.

Because of the small size and operating budgets of such small firms, economic resources simply don't exist to perform research on a company-by-company basis in order to improve process efficiencies, design new environmentally benign or lower-cost products, etc. The cost of environmental compliance is simply passed onto the next customer rather than implementing pollution prevention steps that would eliminate or reduce compliance costs.

2.4.3 Purity Concerns

Recycling in the semiconductor industry entails different concerns than for other manufacturing industries. This is because the purity standards for most input materials to the various process unit operations are extremely rigid. For example, materials with a purity less than 99.999% will generally not be tolerated because they will result in manufactured products that will not meet performance specifications. For most other manufacturing industries, recycled wastes with a 99% purity is exceptionally good, and materials of 90% purity can usually be reused. The question is now being raised in the semiconductor industry, however, as to what material purity is really necessary if the material is being recycled back into its generating process. For example, "wastes" of GaAs consist of nearly 50 percent gallium atoms and the same number of arsenic atoms, with minor amounts of other impurities that may be picked up during the processing steps. If the other, minor impurities are successfully removed, does the purity of the gallium have to be 99.999% with absolutely no arsenic present, provided that the material is to be reused for the growth of GaAs? Would 99.9% be sufficient? Such questions can only be answered by growth and testing of semiconductor compounds and devices using recycled materials in which some residue of the related material is present.

2.4.4 Material Recovery Processes Developed

At the initial stages of the research effort, it was our intent to first address the waste resulting from vapor phase epitaxial growth processes (both VPE and OMVPE). These wastes are in the form of highly toxic chemicals (e.g., arsine, phosphine, organoarsine, etc.) which is usually treated on-site by oxidation in a "hot box" with the oxidized materials scrubbed from the effluent using a water scrubber. This results in generation of wastewaters that must undergo treatment for arsenic removal prior to release to a POTW. However, as our research efforts progressed, it soon became obvious that there were two major reasons for focusing on waste streams other than the wastes from epitaxial growth operations. First, other waste streams, specifically those from foundry operations, constituted a larger and more important "target" for pollution prevention efforts. Second, the development of recovery techniques for the foundry wastewaters also would result in methods for recovery and reuse of materials dissolved in the epitaxy hot-box's scrubber waters. In that way, adoption of a technique with broad applicability in the semiconductor foundries could also allow recovery of epitaxial wastes through an add-on process to the existing waste control methods.

Focusing on the large quantities of arsenic-bearing wastes generated in the III-V foundries, we have developed two processes that can be implemented at foundry sites for the recovery and in-plant reuse of both the very valuable gallium and the highly toxic arsenic that are presently wasted. The first process developed was a thermally-based 3-unit operation process for recovery of both gallium and arsenic from the solid wastes. The wastes processable with this technique include both the large-sized wastes such as boule ends and waste wafers, but also the difficult-to-treat saw fines. Together, these two waste streams account for two-thirds of the arsenic wasted at semiconductor foundries

(approximately 30 to 35% of the arsenic wasted in all of the GaAs semiconductor industry.)

The other process that was developed under this grant is a method for capturing and recovering both gallium and arsenic from the polishing wastewaters. Through use of specific reagents, combined with careful pH and temperature control, the process sequentially removes arsenic from the waste stream and then gallium.   Upon conversion back to metallic arsenic and gallium, the recovered wastes can be further treated for purification using the process developed for the solid waste streams. In fact, the same process used for recovery of oxidized gallium and arsenic from foundry wastewaters can be applied to vapor phase epitaxial scrubber waters. Both of these recovery processes for foundry wastes are described in detail in following sections of this report.